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Evaluation of an open-source nutrient delivery model for estimating pesticide loads in river catchments

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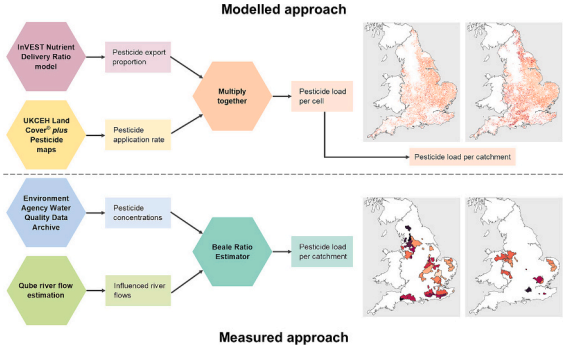
HIGHLIGHTS

- Quantifying pesticide impacts using regularly monitored data is resource-intensive
- The InVEST® NDR model was adapted to estimate pesticide delivery for the first time
- We tested the alignment of these results with loads calculated from measured data
- There were strong positive relationships between measured and modelled loads
- Our modelled method could be used to prioritise catchments for detailed analysis

GRAPHICAL ABSTRACT



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ABSTRACT

Quantifying pesticide runoff hazard in catchments is necessary to predict the impacts and target mitigation. Achieving this at scale through regular, long-term water quality monitoring at multiple sites is time- and resource-intensive. Ideally, such monitoring should be supplemented by models that can estimate pesticide loads in a quicker, less costly manner, especially for unmonitored catchments.

We developed a novel modelling method combining the Integrated Valuation of Ecosystem Services and Tradeoffs Nutrient Delivery Ratio (InVEST® NDR) model and the UKCEH Land Cover® *plus*: Pesticides maps to estimate pesticide load across England. The InVEST NDR model is a widely used, open-source pollutant runoff model, but has not yet been evaluated for use with pesticides. We compared our modelled approach with a measurement-based ("measured") approach. This measured approach used pesticide concentration data from the Environment Agency and river flow data using Qube (a water resource estimation tool) for catchments upstream of the sampling sites: 54 for bentazone and 21 for chlorotoluron.

The significant positive relationships between measured and modelled pesticide loads were stronger when the measured approach accounted for the proportionate area of arable land cover, presumably because the modelled approach only incorporated pesticides from arable sources, explaining up to 90 % of the variation in relative hazard between catchments. Thus, our modelled method forms a flexible approach to mapping relative pesticide

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runoff hazard over large spatial extents, especially where monitoring is limited. It could also be used to rapidly prioritise catchments for more complex analysis to produce accurate measures of absolute loads.

1. Introduction

Pesticides are a major component of modern agriculture and are used to maintain high crop yields and livestock production by reducing the damage caused by pests and diseases. Agriculture is a major land use in Europe, accounting for approximately 40 % (ranging from 7.5 to >70 % per country) in the European Union (Eurostat, 2023), and 70 % land cover in the United Kingdom (UK; Marston et al., 2022). This land is mostly occupied by arable crops and pasture managed for livestock production, and pesticide applications are widespread and commonly used. Pesticides are formulated from many different chemicals, and their interaction with environmental processes (e.g. transportation as runoff) is affected by weather conditions, soil type, and land cover. As a result, they can be difficult to quantify and subsequently control (Campbell et al., 2004; D'Arcy et al., 2000). Pesticides are therefore one of the main sources of diffuse pollution in Europe (European Environment Agency, 2018).

Pesticides in water are widely recognised as problematic: for aquatic ecosystems through toxicity and bioaccumulation, for human health, and for subsequent impacts on the economy (de Souza et al., 2020; Grandjean and Bellanger, 2017; Khalifa et al., 2021; Kim et al., 2017; Morrissey et al., 2015). Policies at local, national, and international scales aim to reduce pesticide pollution and its negative impacts. However, this remains an active issue. In Europe, there has been no overall improvement in ecological status over the past decade under the Water Framework Directive (WFD; European Environment Agency, 2018) due to diminishing returns of existing restoration efforts, and new pressures such as climate change, land-use intensification and emerging contaminants (Haase et al., 2023). For example, neonicotinoid pesticide residues have been observed in non-target organisms (Fuentes et al., 2023; Wintermantel et al., 2020; Woodcock et al., 2021) and surface water (Casillas et al., 2022) despite a 2013 moratorium on neonicotinoid insecticides in the EU.

Efforts to mitigate pesticide runoff thus continue through legislative (e.g. withdrawal of pesticide products), land management (e.g. buffer strips), and technological means (e.g. low drift spraying equipment). To target the application of these efforts and monitor their effectiveness, it is important to be able to predict where pesticide runoff is likely to occur, and to predict the relative hazard across river catchments or subcatchments. Although combining direct measurements of pesticide concentration and river flow is the most accurate way to estimate pesticide load (the total amount of pesticide for a given area over a given period of time, in weight per unit area), generating high-quality and high-frequency measured data is labour-, cost-, and time-intensive across large spatial extents. Conversely, modelling approaches may have lower accuracy but can produce estimates for chemicals in unmonitored areas or across larger spatiotemporal scales. For certain issues, such estimates across larger spatiotemporal scales are critical e.g. understanding the impact of pesticide applications on invertebrate population trends (Mancini et al., 2020).

Many pesticide fate models, which account for the major environmental processes governing pesticide fate, exist for predicting pesticide runoff across space (Commelin et al., 2024). These models or tools can provide in-depth understanding of the movement of individual chemicals and the fine-scale spatiotemporal impacts of environmental processes and management. In a recent review, Centanni et al. (2023) identified 17 tools used to simulate the fate and transport of pesticides. These differ widely in their methods, complexity and intended scale of use: they vary from field to basin scale and encompass a range of pesticides, catchment and management properties. Tools identified include The Soil & Water Assessment Tool (SWAT; Arnold et al., 2012), one of the most commonly used tools across the globe (Centanni et al., 2023), the Pesticide Root Zone Model (PRZM; Carsel et al., 1985), the Integrated Water Quality Model (iWaQa; Honti et al., 2017) and the Model-based approach (Mb risk; Quaglia et al., 2019). SWAT is an open-source integrated catchment model, including a hydrological model and a water quality model, and has been used for a wide range of catchment scales (Centanni et al., 2023). Pesticide fate models can also be combined with complementary models where one alone does not meet the user's goal. For example, PRZM, another commonly used model (Centanni et al., 2023), is designed for field-scale applications but can be coupled with SWAT for watershed- or catchment-level pesticide exposure (Ghebremichael et al., 2022). Similarly, iWaQa, comprising of a substance transfer module and routing module, was initially designed for small streams (Honti et al., 2017) but has been coupled with a model that describes transport and fate in larger rivers to model pesticide concentrations across much of the Rhine basin (Moser et al., 2018). Finally, with the end goal of prioritising mitigation, the Mb risk approach uses field-scale spatial data to identify broader areas of pesticide risk within catchments, but it is not designed to predict pesticide loads (Centanni et al., 2023; Quaglia et al., 2019). Despite the abundance and diversity of tools available, data availability for their implementation and calibration, especially measured pesticide concentrations, remains a significant limiting factor (Centanni et al., 2023). They can also be data intensive in terms of the inputs and parameters required (Moriasi et al., 2007; Neitsch et al., 2011), likely requiring high computational power. These models may thus be unsuitable in data-poor regions or where users require a rapid overview of pesticide hazard across river catchments over large (e.g. national) spatial extents. Choosing a model for simulating pesticide runoff therefore depends on the user's goal in terms of output type, scale and resolution, and data and resource availability.

In recent years, various modelling frameworks have been designed to provide suites of models that produce spatial outputs, are flexible, open source and readily parametrised in data-scarce regions. They are intended to be simple to understand and operate, and balance potential reductions in absolute accuracy with the ability to run multiple models quickly over large spatial extents. One such system is Integrated Valuation of Ecosystem Services and Tradeoffs (InVEST®). The InVEST suite of models (Natural Capital Project, 2023a) aims to quantify and map various ecosystem services, focusing on modelling potential changes across space or under different scenarios. The InVEST Nutrient Delivery Ratio (NDR) model (also referred to in the literature as "Nutrient Retention Model" and "Water Purification Model" in earlier versions) estimates the ecosystem service of nutrient retention by vegetation through calculating nutrient export per grid cell, which can be summed to catchment level (Natural Capital Project, 2023b). The InVEST NDR model has been used worldwide at a variety of spatial scales to quantify nutrient retention ecosystem services over time or under scenarios (Adelisardou et al., 2021; Bagstad et al., 2020; Berg et al., 2016; Finch et al., 2021; Mei et al., 2017), and to understand trade-offs with other ecosystem services (Adelisardou et al., 2021; Sharps et al., 2017; Shi et al., 2021). Studies have quantified InVEST model sensitivities to parameter values and resolution (Anjinho et al., 2022; Benez-Secanho and Dwivedi, 2019; Han et al., 2021, 2020; Redhead et al., 2018; Salata et al., 2017; Sharps et al., 2017; Valladares-Castellanos et al., 2024), performed model validation against measured data (Anjinho et al., 2022; Han et al., 2021; Redhead et al., 2018), and have produced similar estimates of nutrient hotspots compared to those produced by the SWAT model (Cong et al., 2020). The InVEST NDR model was designed to quantify exports, not only for nutrients, but also for any pollutant or contaminant (Natural Capital Project, 2023b). However, to date, its

ability to predict pesticide export has not yet been evaluated in peer-reviewed literature (not present in InVEST literature database (Natural Capital Project, 2024) or searches of scientific literature). In the UK, mapped data on pesticide applications have been produced (UKCEH Land Cover® *plus*: Pesticides maps; Jarvis et al., 2020): these too have not yet been used to estimate pesticide loads in peer-reviewed literature. Combining mapped pesticide applications with the InVEST NDR model thus offers a potential route for rapid assessment of pesticide runoff hazard in UK watercourses. If this method estimates pesticide load with sufficient correspondence to measured values, the InVEST NDR model could be a suitable substitute for more complex models like SWAT, PRZM, iWaQa and Mb risk in more data-scarce regions, or at least sufficient to act as a first pass, to identify areas where the costs of parametrisation and running of more complex models would be best justified.

In this study, we tested the suitability of parametrising the InVEST NDR model for pesticide export and combined it in a workflow with existing national pesticide usage data from UKCEH Land Cover® *plus*: Pesticides to produce mapped estimates of pesticide loads. By comparing our modelled approach against estimated pesticide loads from measured concentrations, we explored the alignment of the two approaches. As a proof of concept, we quantified diffuse source runoff for two pesticides for which measured data were available to evaluate our modelled approach. Our aims were:

1. Modelled approach: to quantify diffuse source agricultural pesticide loads for England using the InVEST Nutrient Delivery Ratio model and mapped estimates of pesticide application rates.
2. Measurement-based (hereon "measured") approach: to quantify diffuse source agricultural pesticide loads for a set of catchments using measured pesticide concentration records and generated river flow data.
3. Evaluation: to assess the similarity between the two approaches for the catchments identified in the measured approach.

We hypothesised that there would be positive coefficients in regressions between pesticide load estimates from the two approaches. We also hypothesised that that adjusting for arable area in the measured approach (to reflect the fact that pesticide data are limited to arable land in the modelled approach) would explain more variation than without this adjustment.

2. Methods

2.1. Data: Pesticide application maps and concentration data

The UKCEH Land Cover® *plus*: Pesticides (LC+ Pesticides) maps (Jarvis et al., 2020) are 1 km resolution raster datasets of estimated total annual applications for 162 pesticide active ingredients across Great Britain (GB), averaged over the period 2012–2017. They are built using high resolution crop maps and national pesticide usage data. For the former, UKCEH Land Cover® *plus*: Crops (LC+ Crops) data were used, derived from Sentinel-1 Synthetic Aperture Radar (SAR) and Sentinel-2 optical satellite data to identify crop types for nearly 2 million land parcels across GB (Upcott et al., 2023). Pesticide usage data were obtained from the Fera Pesticide Utilisation Surveys (PUS; Fera, 2024) and the Scottish Agricultural Science Agency's Pesticide Survey Unit (Scottish Agricultural Science Agency, 2024), collated by Fera. LC+ Pesticides uses aggregated county-level data of reported pesticide usage in terms of total crop area treated, total weight of chemical applied and application rate per active ingredient. Using spatial interpolation to a 1 km resolution, LC+ Pesticides combines LC+ Crops and pesticide usage data to produce continuous coverage maps of average annual pesticide applications across GB.

We used Environment Agency (EA) water quality data from the Water Quality Archive (WQA; previously "Water Information Management System" (WIMS); Environment Agency, 2023a), of pesticide concentration data across England. The WQA holds data collected by the EA of nearly four million samples collected at 58,000 sampling points since 2000 to measure aspects of water quality across England.

2.2. Selecting pesticide active substances

We selected pesticide active substances according to several criteria, based on potential impacts and data availability. Only substances of concern to freshwater environments were considered, as described by the Voluntary Initiative's Water Protection Advice Sheets (The Voluntary Initiative, 2024). Substances selected were used exclusively or predominantly for arable agriculture and not in human or animal medicine, or household products. This was because we were targeting substances that are predominantly emitted by diffuse sources to suit the chosen model and are associated with a single land cover type. Pesticide active substances also needed to be present in the LC+ Pesticides maps. Once data had been acquired, we also applied two further criteria: that they are frequently monitored (detailed in the measured approach, Section 2.6), and that upon removing non-independent overlapping catchments (also detailed in Section 2.6), there were sufficient data to run linear regressions. After applying all criteria, we identified two pesticide active substances with sufficient data: bentazone and chlorotoluron.

2.3. Method: Modelled approach

The modelled approach combined the LC+ Pesticides maps and InVEST NDR model export to generate pesticide loads per 100 m cell. The InVEST NDR model assesses nutrient retention by modelling nutrient export to watercourses from individual grid cells within a catchment. Despite its name, the model was designed to also simulate other anthropogenic contaminants such as agricultural pesticides (Natural Capital Project, 2023b). It uses a mass balance approach combined with empirical relationships to simulate contaminant retention in soil and its transport through surface (and optionally subsurface) flow to a stream. A detailed description of the InVEST NDR model is available elsewhere (Natural Capital Project, 2023b), but here, we provide a brief overview.

In the InVEST NDR model, a user-defined LULC map determines the contaminant export values for every pixel per LULC class. Contaminant transport through the catchment is driven by the local runoff potential (e.g. precipitation), and the initial contaminant load is adjusted to account for transport through the catchment along topographically determined flow pathways. These altered loads may be proportionately split into sediment-bound (surface or, conceptually, shallow subsurface; Natural Capital Project, 2023b) and dissolved (subsurface) contaminants. If no information is available on the partitioning of surface and subsurface contaminants, as was in our case, the user may opt to use only surface flow (Natural Capital Project, 2023b), as has been previously implemented (Anjinho et al., 2022; Benez-Secanho and Dwivedi, 2019; Han et al., 2021; Redhead et al., 2018). Surface NDR is calculated per pixel as the ability of downslope pixels to transport contaminants without retention, using the maximum retention efficiency of the land between the pixel and the stream it flows into (flow path), which is capped at the maximum retention value of the LULC types in the flow path. Finally, an index of connectivity represents hydrological connectivity, as indicated by topography in a digital elevation model (DEM). Contaminant export is the product of the load and the NDR, and the total catchment outlet is the sum of the contaminant export pixels within that defined catchment.

2.4. Method: Measured approach

The measured approach combined pesticide concentration data (EA WQA) with estimated flows to generate pesticide loads for available

upstream catchments, across their shared spatial extent of England, comparable to pesticide loads generated from the modelled approach. Daily flow data and upstream catchments were estimated using Qube (developed by Wallingford Hydrosolutions in collaboration with the Environment Agency). Qube is a best practice tool used by UK and Ireland regulators and water companies to estimate natural and influenced flow statistics and time series in gauged (with gauging stations that systematically record stream flow) and ungauged catchments. The process involved simulating the long-term average flow at previously selected WQA sites. Qube uses the Integrated Hydrological Digital Terrain Model (Morris and Flavin, 1994, 1990) to define the drainage network and the contributing catchment for each location. It then estimates the long term natural and influenced flow statistics, with the natural flows relating to the 1990–2017 catchment abstraction management strategy (CAMS) period of record. This includes the annual and monthly mean flow (Holmes et al., 2002a) and annual and mean monthly flow duration curves (Holmes et al., 2002b).

2.5. Implementation: Modelled approach

The data inputs to the InVEST NDR model are presented in Table 1. All inputs, except the biophysical table, which includes biophysical properties specific to each LULC class and pesticide (Table 2), were the same for both pesticides. Adjustments were first made to the Digital Elevation Model (DEM) to better define the river network and remove DEM artefacts: sinks filled, river network (Moore et al., 2000) etched 10 m deeper to ensure the watercourses and catchment boundaries identified conformed to known actual watercourses and catchments, cell elevation capped at a − 20 m minimum, aggregated to 100 m resolution, and a 1000 m buffer added to edge of the raster with cell values of −20 m elevation to enable accurate catchment capture. The raster used as the nutrient runoff proxy raster was produced using the mean per cell of Had-UK Grid mean annual rainfall datasets for 2000–2017. An offshore pseudo-catchment was created near the origin of the catchments vector to align output rasters to British National Grid 1 km cells, as the version of InVEST used in this study (v3.14.0) aligned outputs to the catchment vector origin, not that of input rasters.

Table 1
InVEST NDR model data inputs, details and sources.

Model data input (data type)	Details	Dataset name and source or value
DEM (raster)	Raster elevation map.	Integrated Hydrological Digital Terrain Model (Morris and Flavin, 1994, 1990)
LULC (raster)	Raster map of LULC classes. All classes have corresponding entries in the biophysical table.	Land Cover Map 2015 (25 m raster; Rowland et al., 2017a)
Nutrient runoff proxy (raster)	Raster map per year of runoff potential: annual precipitation or quickflow index.	Mean per cell of HadUK-Grid mean annual rainfall 2000–2017 (1 km raster; Met Office et al., 2023)
Watersheds (vector polygon)	Vector map of catchment/ watershed boundaries to aggregate model results.	Water Framework Directive Management Catchment Cycle 1 (Environment Agency, 2023b)
Biophysical table (CSV)	Table where each LULC class corresponds to biophysical properties of contaminant load and retention.	See Table 2
Calculate phosphorus retention (true/ false)	Tell model to calculate phosphorus (or other nutrient/contaminant to exclude subsurface modelling) retention and export.	True
Threshold flow accumulation (number)	Using the DEM, the number of upslope raster pixels that must flow into a given pixel before it is classified as a stream.	1000
Borselli K parameter (number)	Calibration parameter determining the shape of the relationship between hydrological connectivity (likelihood of contaminant on pixel to reach the stream) and NDR (percentage of contaminant that reaches the stream). Default is 2.	2

Table 2
Biophysical table of values for bentazone and chlorotoluron for the InVEST NDR model and subsequent analysis in this study. Additionally, critical length of nutrient retention at maximum capacity was 100 m (pixel size) for all LULC classes.

Aggregate class	LULC class	Loading (kg ha^{-1} year^{-1})	Efficiency: bentazone	Efficiency: chlorotoluron
Broadleaf woodland	Broadleaved Woodland	0	0.605	0.675
Coniferous woodland	Coniferous Woodland	0	0.740	0.900
Arable	Arable and Horticulture	1	0.569	0.615
Improved grassland	Improved Grassland	0	0.599	0.665
Semi-natural grassland	Neutral Grassland	0	0.680	0.800
	Calcareous Grassland	0	0.680	0.800
	Acid Grassland	0	0.680	0.800
	Fen, Marsh and Swamp	0	0.680	0.800
Mountain, heath and bog	Heather	0	0.668	0.780
	Heather Grassland	0	0.668	0.780
	Bog	0	0.668	0.780
	Inland Rock	0	0.668	0.780
Saltwater	Saltwater	0	0.500	0.500
Freshwater	Freshwater	0	0.500	0.500
Coastal	Supra-littoral Rock	0	0.647	0.745
	Supra-littoral Sediment	0	0.647	0.745
	Littoral Rock	0	0.647	0.745
	Littoral Sediment	0	0.647	0.745
	Saltmarsh	0	0.647	0.745
Built-up areas and gardens	Urban	0	0.635	0.725
	Suburban	0	0.635	0.725

The biophysical table (Table 2) details LULC- and pesticide-specific values. Aggregate classes were taken from the LCM 2015 1 km dominant aggregate class dataset (Rowland et al., 2017b). As all pesticides used are primarily associated with arable agriculture, of the LULC classes only “Arable and Horticulture” was assigned a loading value. To note, “loading” as referred to in the InVEST NDR model, for instance in the biophysical table, means the same as “application” used in LC+ Pesticides. Here in the biophysical table, we used the loading variable to indicate whether or not a LULC class was subject to pesticide loading, and it thereby acts as a proportion. Retention length is the distance to reach maximum retention efficiency, incorporated to reduce model sensitivity to the LULC raster’s resolution. The model documentation states “In the absence of local data for land uses…you can simply set the retention length constant, equal to the pixel size” (Natural Capital Project, 2023b), so we set it here to the output pixel size of 100 m. “Efficiency” refers to the maximum nutrient or pesticide retention efficiency per LULC class. These efficiency values were calculated as follows. We first calculated a topsoil carbon scaled retention factor (F_i, a proportion) for each LULC aggregate class i (Eq. 1):

$$F_i = \frac{C_i \times 0.8}{C_{max}} \quad (1)$$

where average soil carbon per LULC class (C_i) was derived from Countryside Survey data (Thomas et al., 2020), because pesticide adsorption can be affected by soil organic carbon, which differs between land cover classes. C_{max} refers to the maximum of these values across LULC classes. A scaling factor of 0.8 was used to scale down C_i values below full retention of 1, since we assume that even land cover classes associated with high levels of soil carbon do not retain 100 % of pesticide. Then, per land cover type i and pesticide j, we calculated preliminary maximum retention efficiency ($eff\_p_{i,j}$, Eq. 2, SM Table 1):

$$eff\_p_{i,j} = F_i \times R_j \quad (2)$$

where relative retention values (R_j) of 0.6 and 1 for bentazone and chlorotoluron, respectively, were based on qualitative compound summaries of each pesticide's ability to bind to soil carbon (bentazone: "very high to high mobility" in soil (National Center for Biotechnology Information, 2023a); chlorotoluron: "adsorption dependent on the percentage of organic matter present in the soil… moderate mobility in soil" (National Center for Biotechnology Information, 2023b)). Preliminary analysis suggested that $eff_p_{i,j}$values were too low due to insufficient pesticide retention (SM Table 2). As a result, we proportionately raised the $eff_p_{i,j}$values to produce finalised versions of these ($eff\_a_{i,j}$, Eq. 3, Table 2):

$$eff\_a_{i,j} = eff\_p_{i,j} + \frac{\left(1 - eff\_p_{i,j}\right)}{2} \quad (3)$$

This had the effect of reducing the regression intercept values towards 0 while producing the same coefficients and R^2 values compared to preliminary results (SM Table 2), making them more suitable for use in this study.

The InVEST NDR models were run at 100 m resolution, as previous analyses suggested that finer resolutions than this add little to accuracy at the expense of greatly increased runtime (Redhead et al., 2018). Usually, a user would supply per LULC values representing pesticide loading, but because we have a gridded map of pesticide loading or application (LC+ Pesticides) that allows us to capture far greater variation in loadings than simply assigning the same loading to all arable cells, we set all loading values for arable land to one. Because of this, our model output values for each cell were proportions between 0 and 1, representing the proportion of applied pesticide expected to reach the watercourse. To produce modelled pesticide loads, the 100 m raster of pesticide export proportions (i.e. InVEST NDR model output) needed to be combined with the 1 km LC+ Pesticides maps for each pesticide. Because pesticides were assumed to be applied only to arable land, we evenly split the 1 km pesticide loading value among the 25 m arable cells (using the LCM) within it, and then summed these values to 100 m cells. Each 100 m cell of pesticide export proportion from the NDR model was then multiplied by its spatially correspondent cell of arable pesticide application, generating modelled pesticide runoff or load from each cell across England at 100 m resolution. Once the catchments of interest were finalised (Section 2.6), modelled pesticide loads were summed per catchment to compare with measured loads.

2.6. Implementation: Measured approach

We included data from rivers and streams with at least six records per year, at least three in the wetter six months (August–January) and at least three in the drier six months (February–July), for at least two of the years in the period 2000–2021, to reduce within- and between-year temporal bias while maintaining enough catchments for analysis. This resulted in 210 sites for bentazone and 174 sites for chlorotoluron. Concentration of each pesticide was converted from μg L^{-1} to kg m^{-3}. Catchments in which pesticide concentrations were only given as below detection limits (e.g. "≤ 0.04") were removed from further analysis, as these do not adequately reflect variation in pesticide concentration for calculation of loads.

Daily influenced river flow time series (Young and Jeans, 2019) data from January 2000 to December 2021 were estimated for each of the identified catchments. The artificial influences in England included in Qube corresponded to the Environment Agency Water Resources Geographical Information System (WRGIS) database exported in August 2022. Total daily flow was estimated by multiplying up $m^3\ sec^{-1}$ to $m^3\ day^{-1}$.

We then estimated mean pesticide loads and standard error with the Beale Ratio Estimator (BRE; Beale, 1962) function "beales" from the R package "funtimes" (Lyubchich et al., 2023; R Core Team, 2024). The BRE calculates total pollutant load based on the sample concentrations and the corresponding river flows or discharges. It assumes a constant ratio of load to flow, with the ratio of average load to average flow equalling the ratio of observed load to observed flow for the site and time period of interest. This assumption is not always true, as high flows may carry higher loads immediately after pesticide application than the same high flow later after application, but it is one we acknowledge and is managed in part through our data cleaning methods. BRE is a robust method to use when there are fewer concentration measurements than flow (Beale, 1962), as for our data, and retains the approach used for previous evaluation of the InVEST NDR model in the UK (Redhead et al., 2018).

Some Qube-defined catchments had very small overlaps (2500–7500 m^2) with adjacent catchments. These were handled by assigning the intersected area to the catchment polygon it appeared to be intruding into. The catchments generated by Qube from the sampled points were filtered, owing to large size discrepancies between catchments and catchment nesting, which could result in bias and non-independence of catchments. The largest 5 % and smallest 5 % catchments were first removed to reduce bias associated with atypical catchments. Where the remaining catchments were nested (one inside another), preference was given to catchments where data were available for both pesticides to estimate the validity of the method regardless of the substance selected, otherwise, the outermost catchment was retained. Where catchments were nested but there were two or more inner catchments independent of one another (rather than nested within themselves), the inner catchments were retained to provide more catchments for statistical analysis. Finally, upon examining regression diagnostic plots and statistics, one outlying catchment had a disproportionately high sample quantile for a negligible amount of arable land, whereas a second had an extremely small sample quantile value: these two catchments were swapped for their outer and inner, respectively, nested catchments. This resulted in 54 final catchments for bentazone and 21 for chlorotoluron.

2.7. Evaluation of modelled vs. measured loads

We used linear regressions to assess the relationships between loads estimated via the two approaches, with data transformed using a natural log to correct for skew. We assessed the relationships between the two approaches using a nonparametric test to explore the relationship between relative loads (i.e. ranked data). We used Kendall rank correlation which is slightly more efficient and robust than the Spearman's rank correlation in the presence of outliers (Croux and Dehon, 2010). The Kendall rank correlation assesses the degree of similarity between two sets of paired rank data, to examine the relationships according to the sets' ordinal values. The correlation coefficient, Kendall's Tau (τ), is calculated by dividing the difference between the number of concordant and discordant pairs by their total, giving a value between −1 and 1.

We ran three sets of comparisons: (1) arable area and measured loads, (2) measured loads and modelled loads, and (3) measured multiplied by the proportion of arable area in the catchment and modelled loads. We included an adjustment to the measured load in the

final set of regressions (3) to account for non-arable sources by multiplying the measured value by the proportion of arable land use in the catchment (similar to the adjustment to account for point-source releases of nutrients used in Redhead et al. (2018). Within these sets, we used (a) linear regressions of loads (logged due to data spread) to assess the ability of the model to estimate catchment loads, and (b) Kendall rank correlations of ranked loads to estimate the model's ability to assess relative pesticide hazard.

We expected a relationship between arable area and measured results, since increased runoff where a greater area of the catchment is covered by arable land is a logical expectation for an arable pesticide. Set (1) is therefore a control, equivalent to assessing the catchment pesticide runoff hazard by arable area alone. It might also be expected that some pesticide runoff detected in the measured data may come from sources other than diffuse arable runoff, for example, the use of agricultural pesticides in urban greenspaces, where application rates and subsequent runoff can both be very high (Meftaul et al., 2020). Therefore, we also adjusted our measured loads to try to isolate only the proportion expected to be from arable sources, and thus captured by the modelled approach, giving comparison set (3).

3. Results

There were sufficient suitable data for 54 catchments for bentazone (mean area = 46,050 ha, range = 1689 ha - 193,638 ha) and 21 for chlorotoluron (mean area = 48,293 ha, range = 720 ha - 180,071 ha; Fig. 1.); 7 of these catchments had data for both pesticides. A map of sample site locations in relation to their upstream catchments are in SM Fig. 1, and their coordinates from the EA WQA are in SM Table 3. Fig. 1 shows the modelled loads across England and Wales, the coverage of which reflects the distribution of arable land in England. Using the measured approach, catchments with sufficient data for bentazone covered more parts of England (northwest, central, east and south) than for chlorotoluron (England-Wales border, east, south; Fig. 2). Catchments with higher bentazone per hectare were more concentrated in the northwest, the border of the East Midlands and East of England, and southern England, while catchments with higher chlorotoluron per hectare were similarly located in the south of England (Fig. 2).

Figs. 3 and 4 show linear regression and Kendall rank correlation graphs demonstrating the relationships between the two approaches: between arable area and measured values (models 1a and 1b), measured and modelled values (models 2a and 2b), and measured multiplied by the proportion of arable area and modelled values (models 3a and 3b) for each pesticide. Table 3 provides statistical linear regression results for unranked data and Table 4 provides Kendall rank correlation results for ranked data. There was a weakly positive effect of arable area on measured bentazone loads (Fig. 3, Tables 3 and 4; models 1a and 1b), which was stronger for chlorotoluron (Fig. 4, Tables 3 and 4; models 1a and 1b).

Modelled results were generally higher in absolute terms than measured for both pesticides (Figs. 3 and 4; models 2a and 3a), suggesting that our implementation of the InVEST NDR model generally overestimated catchment pesticide load. For chlorotoluron, the gradients were close to one, so this overestimation was very consistent, whereas this was more variable for bentazone. Adjusting the measured values by multiplying by arable proportion effectively removes the effect of non-arable sources of pesticides, which are not accounted for in the modelled approach. These relationships explained the most variation in the regression models: 70 % for bentazone and 90 % for chlorotoluron (Figs. 3 and 4, Table 3; model 3a), representing a considerable increase for bentazone at over seven times higher compared to model 2a. Preliminary results showed that, while the coefficient and R^2 values remained the same as the main study results in the modelled and measured, the intercept values were higher and further from 0 (SM Table 2). The ranked results also increased in effect size (Figs. 3 and 4, Table 4; model 3b).

4. Discussion

4.1. Comparison of modelled and measured approaches

Our results demonstrate that the InVEST NDR model can be successfully used to predict pesticide loads in watercourses, producing results that show a strong positive correspondence with equivalent values

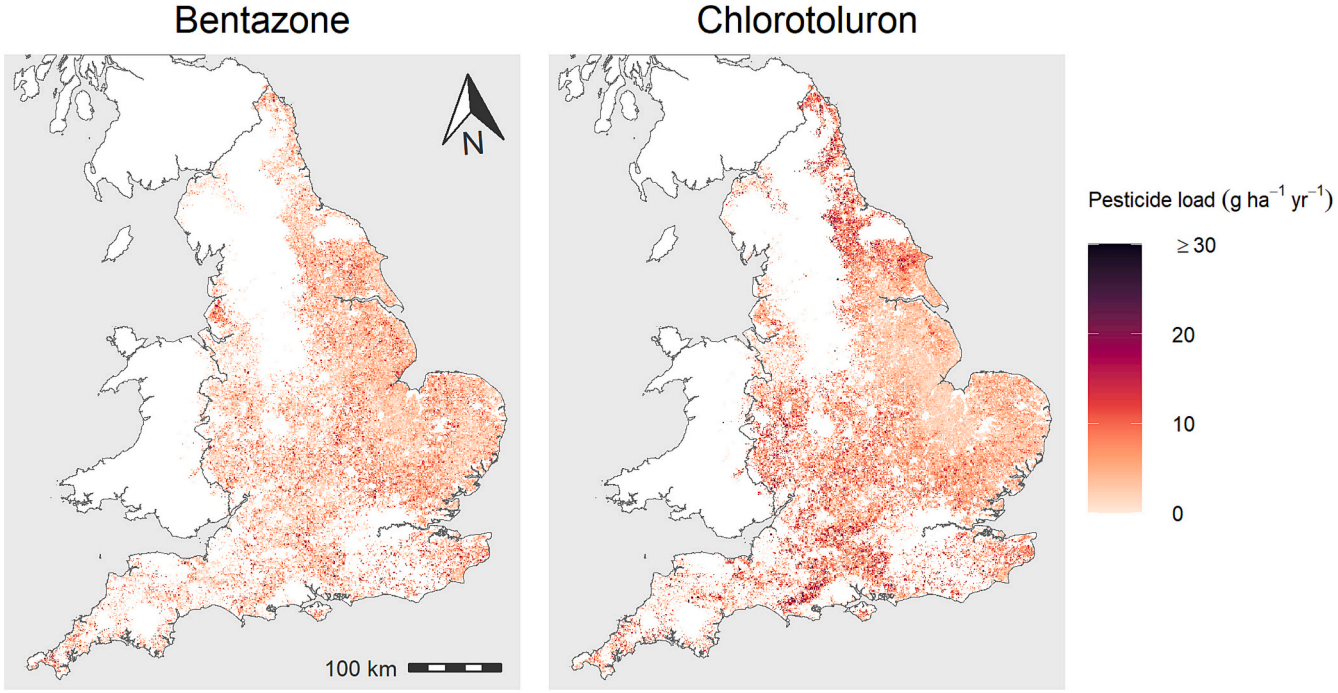

Fig. 1. Modelled pesticide loads at a 100 m resolution. Values were capped at 30 g ha^{-1} yr^{-1} (0.095 % values >30 g ha^{-1} yr^{-1} for bentazone and 0.180 % for chlorotoluron) for ease of interpretation in this figure only.

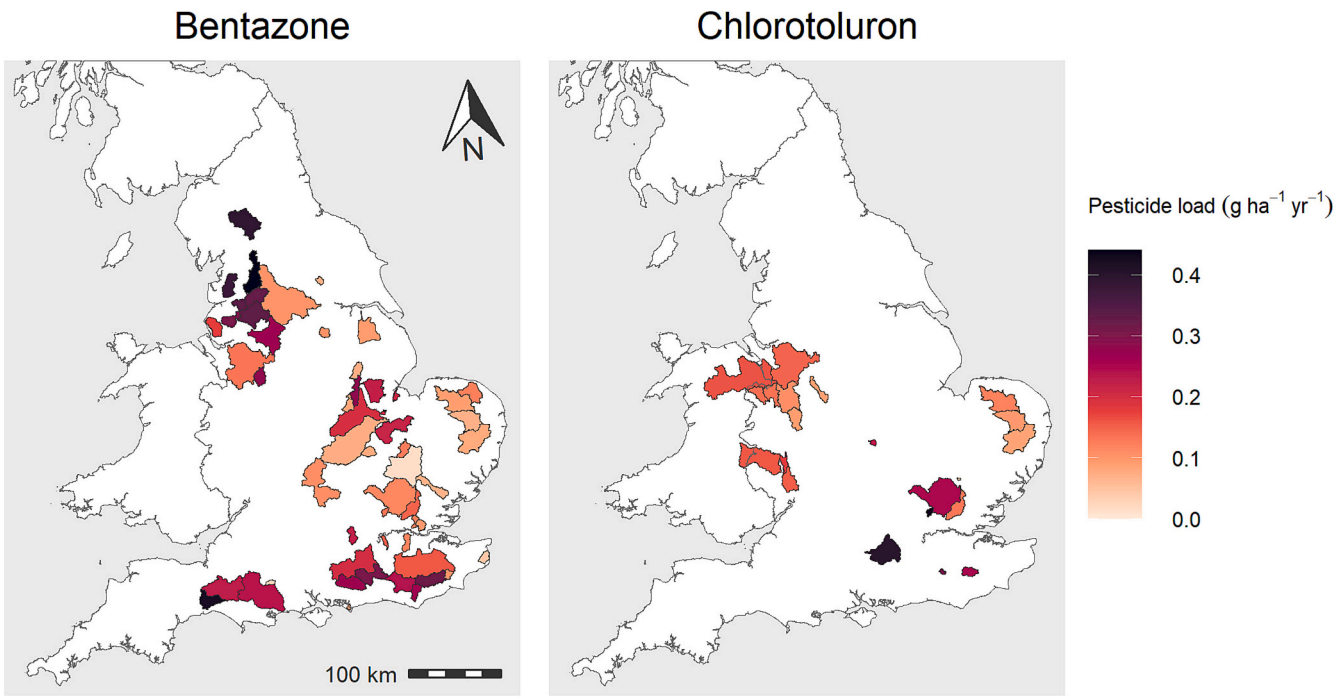

Fig. 2. Measured pesticide loads per hectare for each catchment.

derived from measured data. Several studies have researched other ways in which to improve the prediction of pesticide loads in a catchment when evaluated against measured data, adopting a more passive monitoring approach (Zhang et al., 2016) or a modelling approach (Bach et al., 2001; Holman et al., 2004; Luo et al., 2008; Morselli et al., 2018). However, these studies are often restricted spatially, with loads given at a coarser resolution or only assessing a few catchments. Within this study, we were able to produce estimated pesticide loads at a gridded resolution of 100 m at a national extent. Thus, the InVEST NDR model enables us to estimate loads at the same fine resolution to the full extent of data inputs, including for unmonitored catchments omitted from the measured approach. Reducing pesticide risk through reducing use is often identified as a key facet of increasing farm sustainability (López Rodríguez et al., 2024; Storkey et al., 2024). As national agricultural policy goals aim to improve sustainability (Defra, 2024, 2023), at the same time as meeting other, potentially conflicting targets such as net zero greenhouse gas emissions, or food security, there is a need for models to explore scenarios of change in land management that can indicate trade-offs and synergies between different aspects of sustainability. The reliability of our results, at least relatively between catchments, suggest that the InVEST NDR model could be used to add estimates of pesticide runoff hazard to such assessments, through feeding the model with future scenarios of land use in place of current land use maps (Natural Capital Project, 2023a), alongside the other ecosystem services modelled by the InVEST suite of models.

Converting pesticide load values to ranks brought the relationship between modelled and measured data closer to a 1:1 ratio. Given that the InVEST models are designed to produce results that are indicative of the direction and magnitude of change in ecosystem services under different ecosystem scenarios (Natural Capital Project, 2023a, 2023b), it is not surprising that the results show a stronger correspondence when ranked, assessing the ability of the model to predict relative loading hazard rather than absolute loads; similar results have been found in studies validating InVEST NDR model exports (Redhead et al., 2018) and other InVEST model-derived ecosystem service outputs (Karimi et al., 2021). Thus, our results show that combining the InVEST NDR model with gridded estimates of pesticide application can give estimates of relative load hazard that show a similar correspondence to measured pollutant data, as do other InVEST models which have been evaluated over large spatial scales (e.g. water yield (Gosal et al., 2022) and nutrient runoff (Redhead et al., 2018)). This means our modelled approach could be used to make reliable estimations of relative pesticide load hazard across the landscape, even where measured pesticide concentration records are absent, although further exploration of the approach would be valuable given that other studies have found variability (Sharps et al., 2017) or consistent underestimation (Berg et al., 2016) in InVEST NDR model results compared to measured equivalents.

4.2. *Strengths and limitations of the modelled approach*

For both pesticides that we studied, regression variation was best explained when the measured load was adjusted to account for non-arable sources. Improvements in the relationship with this adjustment in place demonstrates the value added by the model's inputs and processes. This both increased the amount of variation explained and resulted in regression coefficients closer to one, especially for bentazone. Even though we selected pesticides that are predominantly used in arable settings, bentazone may be used in amenity grasslands and industrial turfcare settings (EFSA, 2015), which are not accounted for in the LC+ Pesticides data, nor does amenity grassland belong to its own independent LCM class on account of it being land use and not land cover. An adjustment to the model could be made if average application rates for such uses were available (or if the gridded pesticide application data encompassed these uses). We note that for chlorotoluron, which is more restricted to cereal crops and therefore to the LCM's arable land cover class than bentazone, the impact of adjusting for arable area was much lower. This difference in the purity of pesticide usage per land cover type is likely the cause of high measured bentazone estimates in some catchments in the northwest of the country, where arable coverage was disproportionately small (indicated by sparser cells of modelled estimates). Here, it is possible that bentazone is applied more to improved grassland than in other catchments, as seen in another grassland-heavy catchment (Khan et al., 2020). Additionally, the LC+ Pesticides dataset was created through processes including interpolation (Jarvis et al., 2020), which resulted in some high outlying values where modelled pesticide load was spatially coincident with areas of

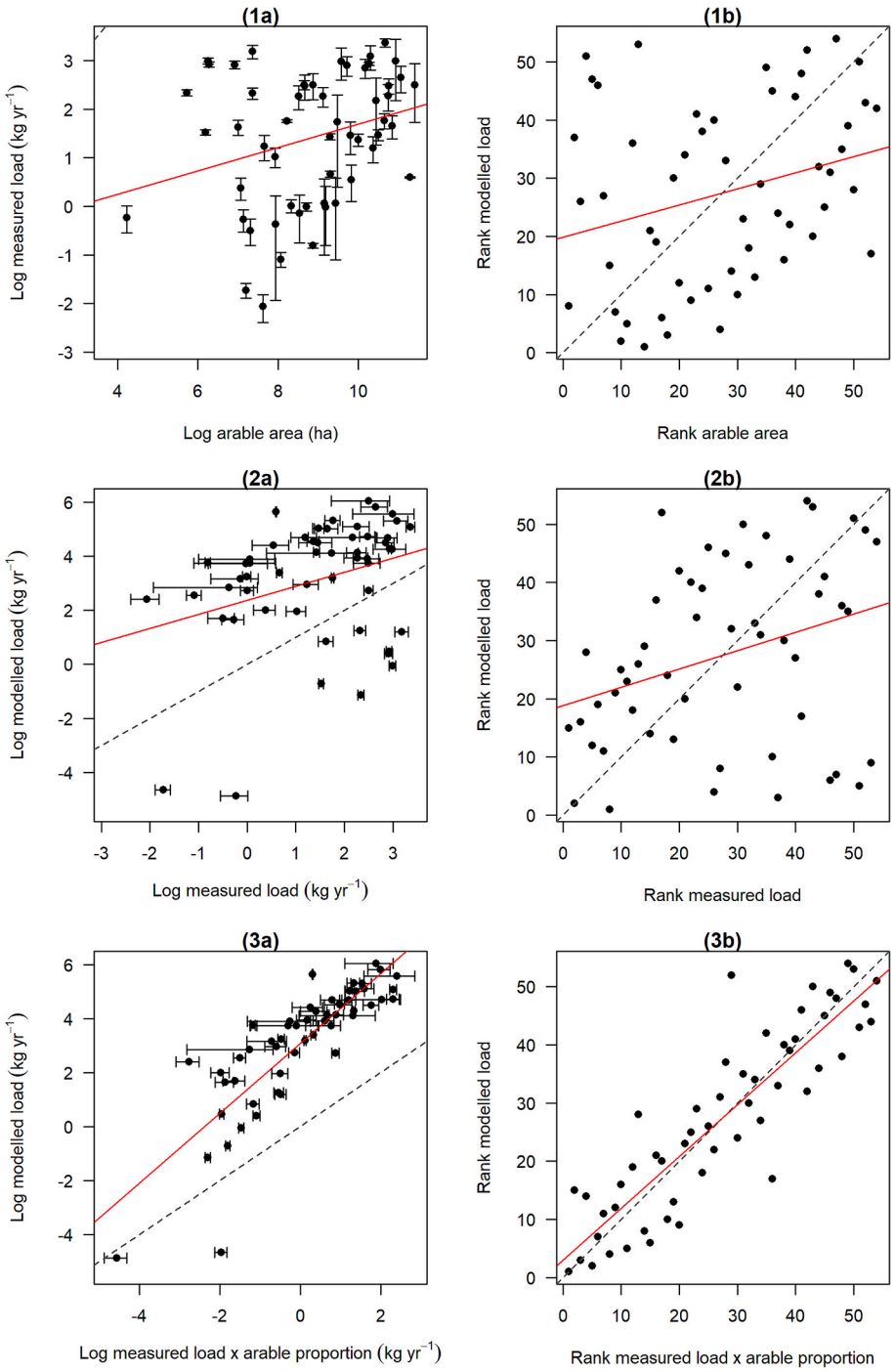

Fig. 3. Linear regressions and Kendall rank correlations for bentazone. Solid red lines show linear regression (a) and Kendall rank correlation (b) results, and dashed grey lines show a coefficient of 1 at intercept 0 (1:1 ratio). All relationships are significant at $p < 0.05$, but the strength of these relationships varies widely (Tables 3 and 4). Standard error data were available for the measured approach only and are shown as error bars.

proportionately less agriculture. However, these constituted only a very small (< 0.2 % over 30 g ha^{-1} yr^{-1}) proportion of modelled load values. The LC+ Pesticides dataset allow for spatial variability in pesticide loads within the arable land cover class and thus should increase the accuracy of the model beyond the default InVEST NDR model approach (which would apply a uniform loading coefficient for all arable cells). In regions without an equivalent pesticide application map, or pesticide usage data and a crop map to create one, this default approach may be the only one available, although subclasses of arable land could be created to allow pesticide loads to vary by crop rotation, management type or sub-region, where these data exist.

While modelled pesticide loads show a strong, positive relationship with measured loads, modelled pesticide loads per catchment were generally greater than measured loads. This might be expected, given the simplicity of our modelling approach and the InVEST NDR model. In effect, this model takes a "worst case scenario", assuming that all pesticides applied to a 1 km cell are available for potential surface runoff and that no further reduction of the original pesticide load takes place once a pesticide leaves the cell (although it can be retained by downstream cells). As bentazone and chlorotoluron are applied as post-emergence products, some active ingredients will be intercepted by the crop canopy and target weed species. Subsequent pesticide fate is

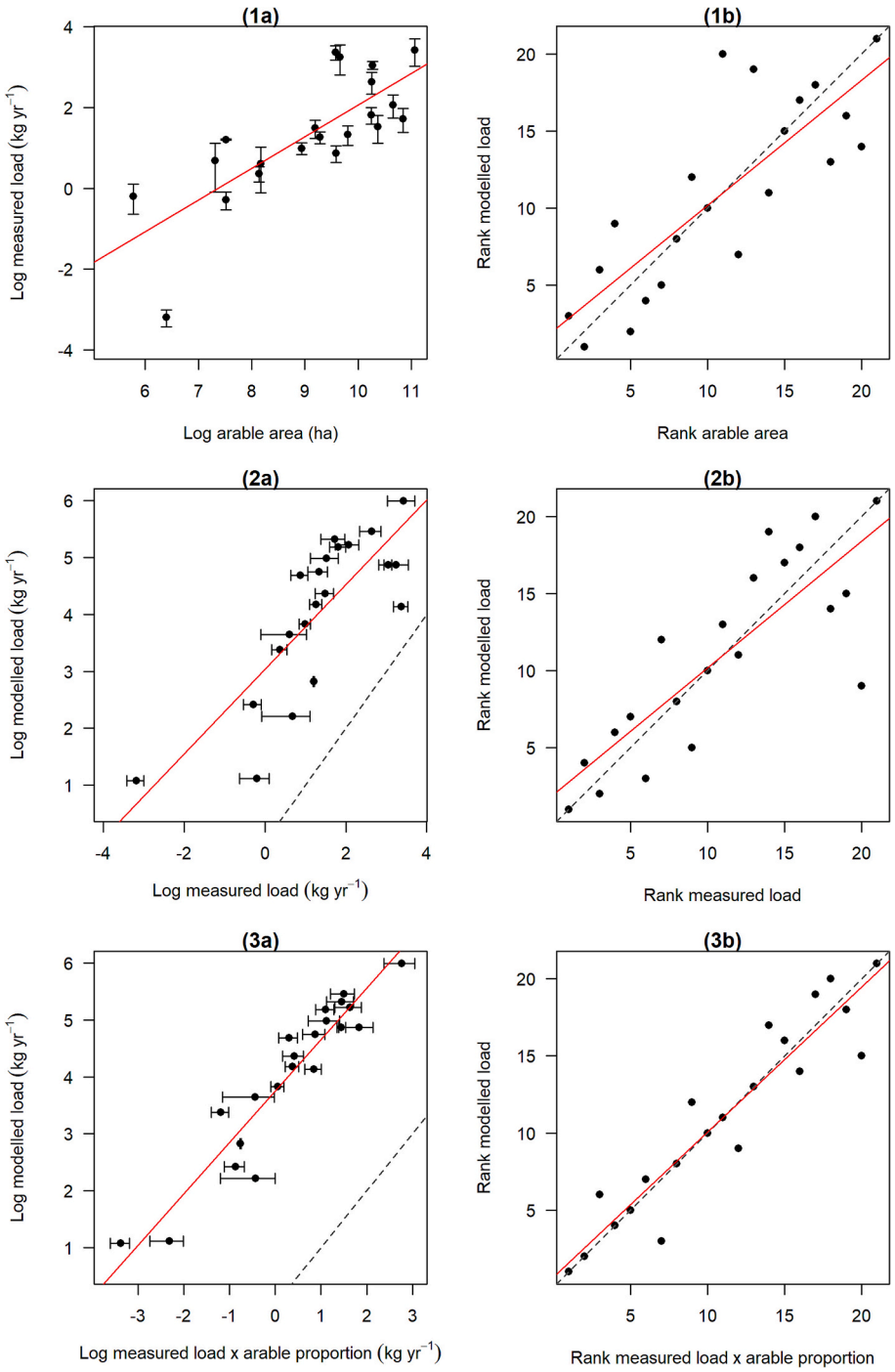

Fig. 4. Linear regressions and Kendall rank correlations for chlorotoluron. Solid red lines show linear regression (a) and Kendall rank correlation (b) results, and dashed grey lines show a coefficient of 1 at intercept 0 (1:1 ratio). All relationships are significant at $p < 0.05$, but the strength of these relationships varies widely (Tables 3 and 4). Standard error data were available for the measured approach only and are shown as error bars.

Table 3
Linear regression results.

Pesticide	Model	Description	Coefficient	Intercept	p	R^2
Bentazone	(1a)	Log arable area vs. log measured	0.24	−0.72	0.039	0.07
($N = 54$)	(2a)	Log measured vs. log modelled	0.52	2.37	0.022	0.10
	(3a)	Log (measured × arable proportion) vs. log modelled	1.29	3.08	< 0.001	0.70
Chlorotoluron	(1a)	Log arable area vs. log measured	0.78	−5.78	< 0.001	0.60
($N = 21$)	(2a)	Log measured vs. log modelled	0.74	3.03	< 0.001	0.65
	(3a)	Log (measured × arable proportion) vs. log modelled	0.90	3.75	< 0.001	0.89

Table 4
Kendall rank correlation results.

Pesticide	Model	Description	z Coefficient	p	τ
Bentazone (N = 54)	(1b)	Rank arable area vs. rank measured	2.19	0.029	0.21
	(2b)	Rank measured vs. rank modelled	2.48	0.013	0.23
	(3b)	Rank (measured x arable proportion) vs. rank modelled	7.63	< 0.001	0.71
Chlorotoluron (N = 21)	(1b)	Rank arable area vs. rank measured	170	< 0.001	0.62
	(2b)	Rank measured vs. rank modelled	175	< 0.001	0.67
	(3b)	Rank (measured x arable proportion) vs. rank modelled	189	< 0.001	0.80

then governed by complex interactions between soil, water and biological activity (Gosal et al., 2022). Though nutrients degrade over time, the chemical processes, factors affecting degradation and timeframe are different for pesticide degradation, resulting in half-lives varying from days or weeks to months in soil (National Center for Biotechnology Information, 2023a, 2023b). The InVEST NDR model in its current state does not account for the complexities of nutrient degradation, let alone pesticide degradation. Indeed, it is the complexity of these processes and the difficulty in obtaining the necessary parameters to run models of pesticide fate over large spatial extents that led us to explore whether a simpler approach can at least predict the relative pesticide runoff hazard, perhaps akin to the Mb risk map (Quaglia et al., 2019). Future research could involve comparing results from our modelled approach using the InVEST NDR model with those as generated by the SWAT model, which can account for degradation (Neitsch et al., 2011) and may give improved estimates. Some studies have compared outputs produced by InVEST models and SWAT, with one study demonstrating general consensus between hotspots estimated by the InVEST NDR model and SWAT (Cong et al., 2020). These studies recommend that choice of model depends on purpose and geographical context (Cong et al., 2020; Dennedy-Frank et al., 2016).

The InVEST NDR model does not take soil type as an input. Soil type is relevant to diffuse source pollution estimations (Campbell et al., 2004) because soil adsorption depends on soil organic carbon, and soil organic carbon differs between land cover classes. Therefore, we based our retention factors on scaled soil carbon estimates per land cover class (Thomas et al., 2020). The likely reality is that soil type varies within land cover classes, but we cannot incorporate this variability into the InVEST NDR model. The model also cannot account for certain catchment-specific physical properties, as demonstrated by the variation in catchments' responses when changing the Borselli K parameter (Redhead et al., 2018). There is a general lack of empirical data on pesticide retention rates at the land cover class scale for England, less still that differentiate between surface and subsurface flow and so potentially limited our modelled approach in this way. This is particularly important given the InVEST NDR model sensitivity to inputs identified in previous research (Anjinho et al., 2022; Benez-Secanho and Dwivedi, 2019; Han et al., 2021, 2020; Redhead et al., 2018; Salata et al., 2017; Sharps et al., 2017), as different data sources or choices of calculations may produce different outputs to those we produced in this study. In preliminary analyses, using lower pesticide retention values than in this study, we saw weaker relationships between the two approaches. While the gradients remained the same, the modelled intercepts were greater than the measured and even further from 0. This again alludes to the sensitivity of the InVEST NDR model to its input values. It would be possible to further calibrate this model for a more true-to-life output with careful consideration of model-sensitive inputs; while studies focus on calibrating the model's Borselli K and Threshold Flow Accumulation calibration parameters (Han et al., 2021; Redhead et al., 2018; Valladares-Castellanos et al., 2024), less is known about the effects of calibrating the model's other input values, which may also affect model estimates (Valladares-Castellanos et al., 2024). These could include values in the biophysical table, spatial input data, and the ratio of surface to subsurface flow per pesticide active ingredient from the model workbench, or the relative retention values and carbon scaling factor which we also used here. However, this lies beyond the scope of this study. There are also dangers in calibrating the model close to the measured data, since the measured data do not necessarily represent a true picture of pesticide loads.

4.3. Strengths and limitations of measured data

Our results are not a true validation of the model, instead being an evaluation of the model against estimated loads, which are themselves not likely to be fully accurate representations of the total pesticide load in a catchment, for a number of reasons. Firstly, loads were calculated from measured concentrations and generated flows: there is an element of modelling in the measured approach. We decided to obtain flow data using Qube rather than other methods, e.g. the National River Flow Archive (NRFA; Dixon et al., 2013) as used in Redhead et al. (2018). Qube can estimate flows in both gauged and ungauged catchments, allowing flows to be generated precisely where required, unlike NRFA data which must be spatially coincident with EA WQA sites to calculate pollutant loads. Qube is also a best practice tool used by UK government agencies and water companies, so it is trusted as a quality tool to generate real-world flows across the country. Secondly, there were far fewer concentration records than flow data, with generated flow data available daily but concentration samples taken less frequently. Therefore, concentration values would only be truly indicative of those moments in time. Thirdly, the inconsistency of concentration samples taken across different catchments means that some catchments may be more "true-to-life" than others. While some sites were sampled less than monthly, others were sampled biweekly; some in only a couple of years while others for most of two decades. This may have introduced within-year or between-year bias where there were fewer concentration records, which could shift averages more in favour of abnormal values. However, we considered the BRE would be suitably robust for our method as it has been shown to perform better than other estimators in terms of bias and efficiency (Swain and Dash, 2020), even with low sampling frequency (Lee et al., 2016). Fourthly, while we accounted for non-arable applications and/or point-source pesticide releases by including the arable proportion in our calculation, we assumed that loads per unit arable area are the same as those per unit non-arable area. While this is similar to previous handling of point-source data (Redhead et al., 2018), there remains difficulty in accurately quantifying arable vs. non-arable and diffuse-source vs. point-source pesticide loads.

There are also limitations in the steps required to convert measured concentrations to total annual loads. Although we aligned data years as much as possible while reducing bias from fluctuations, a complete temporal overlap between shorter-term data (LCM products, WFD data) with longer-term data (Qube, WQA, HadUK-Grid) was not always possible. In assessing the WQA data, we found that concentrations were often recorded using a minimum threshold value of detection (e.g. "<0.04"). At some sites, a plateau of a single threshold value existed through all records, while others had more than one threshold value, as different detection thresholds applied over time: these results were omitted from our study but did substantially decrease the amount of usable data. While the Beale Ratio Estimator is designed to work with missing data, our measured results would be more accurate if there were more high-precision concentration data available, and our ability to calibrate the model and explore the alignment of measured and modelled approaches under different situations (e.g. for smaller vs larger catchments, or additional pesticides) would be improved. An alternative to using measured concentration and generated flow data

would be to measure both, such as combining the EA WQA with NRFA data. However, this would likely further reduce the number of catchments with sufficient data if both records were not taken simultaneously. Ultimately, these issues demonstrate the challenge of relying on measured data, and the need for reliable models – measured data are, due to cost and time constraints, inevitably patchy.

5. Conclusions

Pesticide sampling campaigns are costly in time, money and effort, and are thus often restricted in space and time (in both length and frequency of record). Therefore, we must rely on more efficient modelled approaches for a large-scale picture of pesticide loads in both monitored and unmonitored catchments, and over a longer timeframe. Our study presents the view that the InVEST NDR model is a useful tool to use in making these estimations, at least where a rapid assessment of relative pesticide loadings to water between catchments is the desired outcome. If the end goal is to produce closer to a 1:1 ratio of measured to modelled results, so that the model could be used as a proxy for the measured, further work must go into and calibrating our model and evaluating its performance, in part through closer examination of retention rates in the InVEST NDR model. Although future work may strengthen our modelled approach and increase its accuracy, our model in this study already provides a good indication of the relative pesticide runoff hazard across and within catchments when we use ranked data, so could be accepted as a "worst case" hazard estimate. Our approach is, therefore, potentially useful for informing policy concerning the reduction and mitigation of pesticides in the environment, especially in terms of high-level spatial targeting or scenario exploration across a multi-catchment region of interest (Weissteiner et al., 2014). This can then be used to target and prioritise more detailed work for catchments identified as showing greater relative pesticide hazard. At these smaller spatial scales targeted measuring campaigns become more feasible and the data required to parametrise more complex models (e.g. SWAT) are more likely to be available. Our modelling approach thus adds a potentially valuable tool to the existing pool of ecosystem service models for assessing agricultural sustainability, for other regions, nations and countries with sufficient data on pesticide use.

CRediT authorship contribution statement

Emily V. Upcott: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Virginie Keller:** Writing – review & editing, Project administration, Conceptualization. **Daniel S. Read:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Clarissa Rizzo:** Writing – review & editing, Writing – original draft, Resources, Methodology, Data curation. **Jude Jeans:** Resources, Conceptualization. **John W. Redhead:** Writing – review & editing, Supervision, Project administration, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2025.179223.

Data availability

The majority of data used in this project is available (cited in paper). In some cases, a licence may be required to access data (e.g. Qube, CEH Land Cover® plus: Pesticides).

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